INTERSTELLAR METHYL MERCAPTAN

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Received 1979 June 14; accepted 1979 July 18

ABSTRACT

Methyl mercaptan (CH_3SH) has been identified in Sgr B2 from observations of six lines in its millimeter-wave spectrum. The CH_3SH rotational temperature and column density in Sgr B2 are $T_{rot} = 9 \pm 3$ K and $N = 1.5 \pm 0.2 \times 10^{14}$ cm^{-2}, respectively. The CH_3SH/CH_3OH ratio is apparently not greatly different from the cosmic S/O ratio.

Subject headings: interstellar: molecules

Sulfur compounds are prevalent in interstellar molecular clouds (Table 1) and constitute the most important exception to the finding that interstellar molecules are composed of only four elements from the first two rows of the periodic table: H, C, N, and O. In spite of differences which presumably exist in space between the chemistries of sulfur and oxygen, a simple rule of thumb has proven effective in searching for new sulfur molecules, namely, that the abundance of a sulfur compound relative to its oxygen analog is roughly equal to the cosmic S/O ratio, 1/42. Here and in an accompanying *Letter* we report the detection in Sgr B2 of two new sulfur molecules satisfying this rule: methyl mercaptan CH_3SH and isothiocyanic acid HNCS—the sulfur analogs of methyl alcohol and isocyanic acid, two of the more abundant interstellar oxygen molecules. A malodorous gas found in certain deposits of petroleum and natural gas and among the products of organic metabolism, methyl mercaptan is used industrially in the synthesis of many compounds, in particular the amino acid methionine. With six atoms, it is the most complicated sulfur molecule yet detected in space.

Like methyl alcohol, methyl mercaptan is a molecule with hindered internal rotation, and its rotational levels similarly consist of noncombining torsional symmetry species A and E (Lees and Baker 1968; Lees 1973). The lower rotational levels of CH_3SH and the transitions we have observed are shown in Figure 1. Figures 2 and 3 and Table 2 summarize the observational data.

Our first indication of methyl mercaptan was the line at 75,863 MHz in Figure 2, detected in 1978 May during a survey of the spectrum of Sgr B2 with a cryogenic 60–90 GHz receiver (Linke, Schneider, and Cho 1978) on the new 7 m telescope of Bell Telephone Laboratories at Holmdel, New Jersey. Attempts to find a reasonable transition of a known interstellar molecule to match this line failed. Subsequently, from calculations based on laboratory spectroscopy at centi-

meter wavelengths (Kilb 1955), and on direct laboratory measurement (Johnson 1979), we were able to identify it as a blend of the $J_K = 3_0 \rightarrow 2_0$ transitions of the A and E symmetry species of methyl mercaptan.

Since by this time an equally sensitive 90–140 GHz receiver had been installed on the telescope, we proceeded to confirm this identification by finding the next set of rotational transitions, $J = 4 \rightarrow 3$, lying in the vicinity of 101 GHz. Ultimately, as Figure 3 shows, we detected all the $4 \rightarrow 3$ transitions appreciably excited in Sgr B2—a total of six transitions forming five well-resolved lines (the $K = 0$, A and E lines are again blended).

Kilb's (1955) data and a calculation of the rotational spectrum kindly provided by R. Lees were instrumental in identifying the $4 \rightarrow 3$ lines, but as some of the calculated rest frequencies were uncertain by several MHz, we subsequently measured them all with a free space millimeter-wave spectrometer at the Columbia Radiation Laboratory. The theoretical spectrum in Figure 3 and most of the rest frequencies and radial velocities in Table 2 are based on this new laboratory data. All radial velocities are about 60 km s^{-1}, the same as many other molecules in Sgr B2, and relative intensities are normal. The overall agreement of theory with observation is so good that methyl mercaptan qualifies as one of the most securely identified interstellar molecules.

In the course of our observations it was brought to our attention that Turner (1977) had already observed the line at 101,139 MHz in Sgr B2, and had suspected it to be methyl mercaptan, but had been unable to confirm this identification by observing the satellite lines. With hindsight it is possible to see that one satellite line is actually present in his data. As can be seen by comparing our Figure 3 and his Figure 2, the wide line at 101,036 MHz attributed by Turner to ketene is actually a blend of ketene and one of the $J = 4 \rightarrow 3$ transitions of methyl mercaptan.

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Because our observations sample rotational levels at various energies above ground, they determine fairly precisely the rotational partition function of methyl mercaptan, and hence its rotational temperature and column density. Figure 4 is essentially a standard log intensity versus rotational energy plot of the data in Table 2, fitted by the linear relation expected for optically thin emission lines from rotational levels in

TABLE 1

INTERSTELLAR OXYGEN AND SULFUR MOLECULES

CO.................	CS
SiO................	SiS
NO................	NS
OH.................	(SH)
(O_2).............	SO
(CO_2)............	OCS
H_2O.............	H_2S
(O_3).............	SO_2
HCO^+............	(HCS^+)
HCO..............	(HCS)
HNO..............	(HNS)
H_2CO............	H_2CS
HNCO.............	HNCS
HCOOH............	(HCOSH, HCSOH)
H_2CCO...........	(H_2CCS)
NH_2CHO..........	(NH_2CHS)
CH_3OH...........	CH_3SH

NOTE.—Left: interstellar oxygen molecules with six atoms or fewer; right: all interstellar sulfur molecules observed to date. Molecules in parentheses have not been detected.
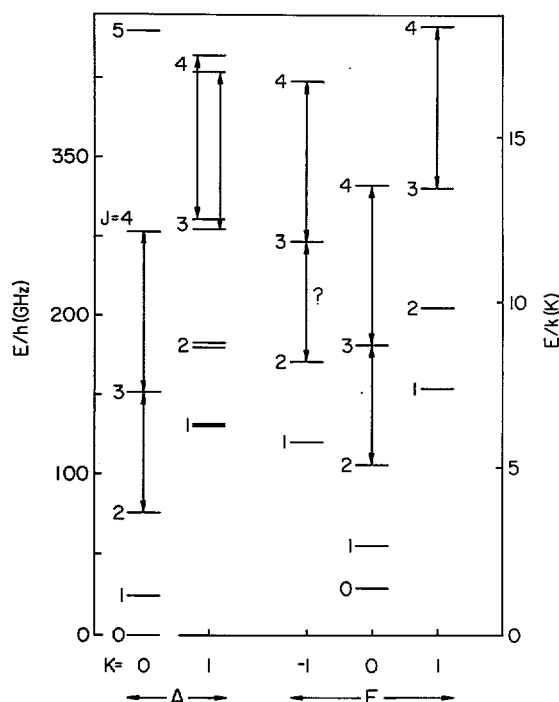

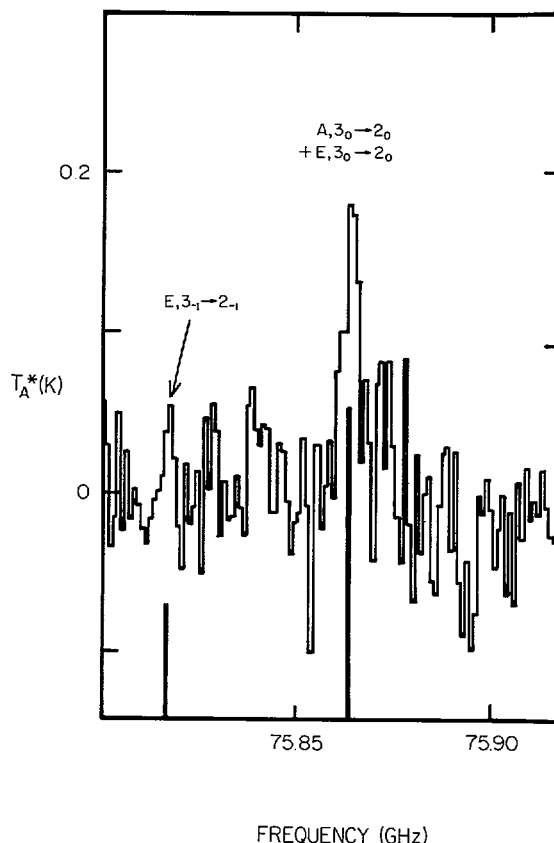FIG. 1.—Lower rotational levels of CH_3SH, showing transitions observed in Sgr B2.

FIG. 2.—$J = 3 \rightarrow 2$ transitions of CH_3SH in Sgr B2, observed at a spectral resolution of 1 MHz. The theoretical spectrum of CH_3SH (vertical bars) has been calculated from T_{rot} and N in equations (2) and (3), and $v_{LSR} = 62$ km s^{-1}.

thermal equilibrium:

$$\log\left(\frac{3k\langle\Delta v T_A^*\rangle}{8\pi^3\nu S\mu_a^2}\right) = \log\left(\frac{N}{Z}\right) - \frac{E\log e}{kT_{rot}} \quad (1)$$

Here S is the line strength, $Z \approx 2[\pi(kT_{rot}/h)^3/ABC]^{1/2}$ is the rotational partition function, and $\langle\Delta v\, T_A^*\rangle$ is the line equivalent width ($1.06\, T_A^*\, \Delta v$ for a Gaussian line whose full velocity width at half-intensity is Δv).

The linearity of the plot in Figure 4 implies the existence of rotational equilibrium and also confirms the assumption of low optical depth. A least-squares fit of equation (1) to the data yields for the rotational temperature of methyl mercaptan,

$$T_{rot} = 9 \pm 3K, \quad (2)$$

and for its column density,

$$N = 1.5 \pm 0.2 \times 10^{14}\,cm^{-2}. \quad (3)$$

Uncertainties are 1 σ.

No correction in deriving equations (2) and (3) has been made for the difference in antenna beamwidth at 76 and 101 GHz—it has tacitly been assumed that the source fills the beam, and T_{rot} and N are averaged over

the $2''0$ antenna beam at 101 GHz. If the source is instead pointlike, beam correction raises the low E/k point in Figure 4 to the X-position, T_{rot} drops as a result by 2.4 K, and N rises by 14%—essentially small corrections.

It is worth noting that T_{rot} is less than some other molecular temperatures in Sgr B2, for example, the brightness temperature of CO (30 K; Linke, Stark, and Frerking 1979), or the excitation temperature of

NH_3 (36–73 K; Morris *et al.* 1973). Whether this means that methyl mercaptan exists in a region of very low kinetic temperature in Sgr B2, or is instead subthermally excited, is a moot question that cannot be decided without more data. We have not as yet investigated the distribution of CH_3SH in Sgr B2, and so know nothing of the extent of the source.

According to Gottlieb *et al.* (1979) the column density of methyl alcohol in Sgr B2 is 2×10^{16} cm^{-2}, implying

TABLE 2

METHYL MERCAPTAN IN SAGITTARIUS B2[a]

Transition	ν_0 (MHz)	$T_A{}^*$ (K)	v_{LSR} (km s^{-1})	Δv (km s^{-1})
E, $3_{-1} \rightarrow 2_{-1}$	75,816[b]	~ 0.05	...	22
A, $3_0 \rightarrow 2_0$	$75,862.87 \pm 0.07$[c]			
E, $3_0 \rightarrow 2_0$	$75,864.43 \pm 0.07$[c]	0.19 ± 0.03	62 ± 3	22 ± 8
A+, $4_1 \rightarrow 3_1$	$100,110.27 \pm 0.04$	0.06 ± 0.02	60 ± 3	15 ± 9
E, $4_{-1} \rightarrow 3_{-1}$	$101,029.75 \pm 0.05$	~ 0.10	...	...
A, $4_0 \rightarrow 3_0$	$101,139.16 \pm 0.05$			
E, $4_0 \rightarrow 3_0$	$101,139.65 \pm 0.04$	0.27 ± 0.02	61 ± 1	22 ± 2
E, $4_{-2} \rightarrow 3_{-2}$	$101,167.15 \pm 0.04$			
E, $4_2 \rightarrow 3_2$	$101,168.34 \pm 0.04$	< 0.05	...	...
E, $4_1 \rightarrow 3_1$	$101,284.36 \pm 0.04$	0.09 ± 0.02	60 ± 3	16 ± 5
A−, $4_1 \rightarrow 3_1$	$102,202.49 \pm 0.04$	0.08 ± 0.01	61 ± 2	18 ± 7

NOTE.—$T_A{}^*$, v_{LSR}, and Δv (full width at half-intensity) have been determined by a least-squares fit of Gaussian line profiles to the observational data in Figs. 2 and 3. Uncertainties are 1 σ.

[a] $\alpha(1950) = 17^h44^m11^s$, $\delta(1950) = -28°22'30''$.

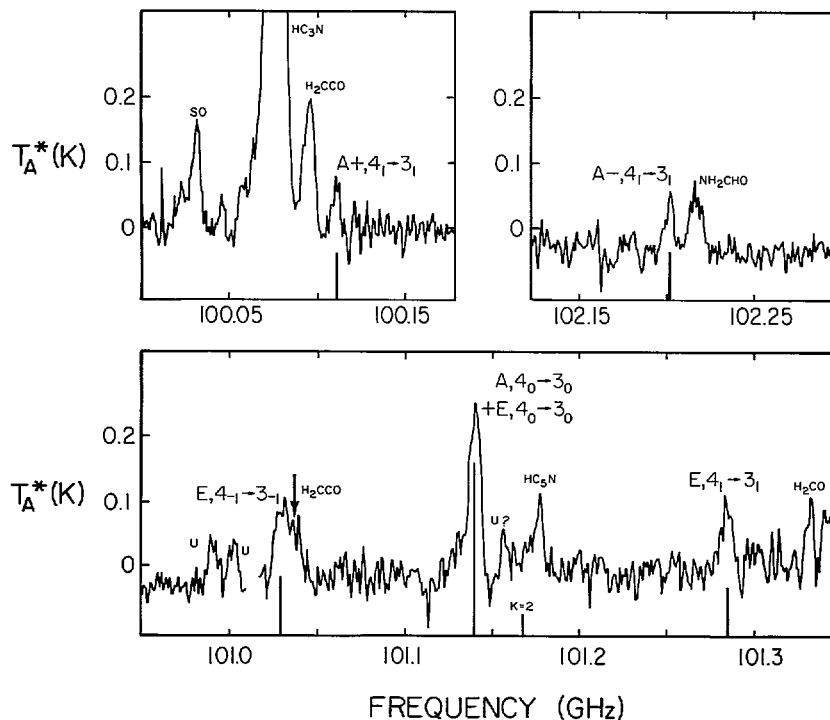[b] Calculated by Lees (1973).

[c] Measured at NBS by Johnson (1979).

FIG. 3.—$J = 4 \rightarrow 3$ transitions of CH_3SH in Sgr B2, observed at a spectral resolution of 1 MHz. As in Fig. 2, the theoretical spectrum (*vertical bars*) has been calculated from T_{rot} and N in equations (2) and (3), and $v_{LSR} = 62$ km s^{-1}.
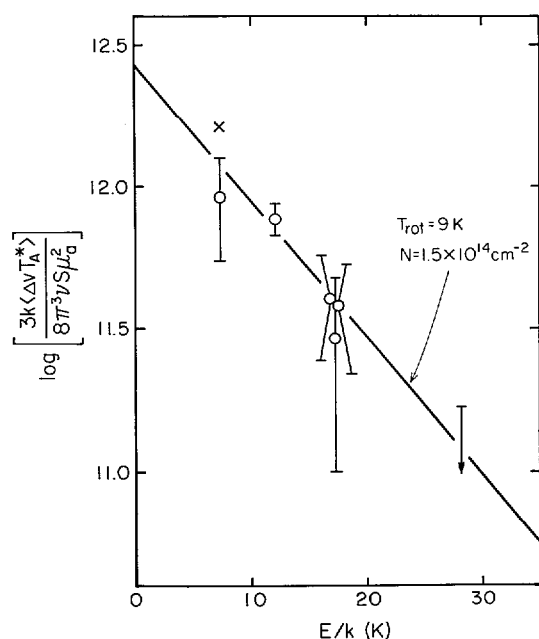
Fig. 4.—Log intensity versus rotational energy plot for CH$_3$SH in Sgr B2. Upper limit at lower right derives from the missing $K = 2$ line in Fig. 3.

a CH$_3$SH/CH$_3$OH ratio R of 1/130, or one-third the cosmic S/O ratio. However, R is probably uncertain by a factor of at least 2, owing to uncertainty in the column density of methanol, and to the difference between our beamwidth and that of Gottlieb *et al.* (1979). Methyl mercaptan is therefore apparently a fairly good example of the rule that the ratio of an interstellar sulfur molecule to its oxygen analog is close to the cosmic S/O ratio.

No systematic attempt has yet been made to find methyl mercaptan in other sources, except Ori A. There we have obtained an upper limit of 0.1 K for the strongest $J = 4 \rightarrow 3$ line at 101,139 MHz (this limit represents the peak-to-peak noise at a spectral resolution of 250 kHz). Assuming an excitation temperature of 70 K and a line width of 4 km s^{-1}, it follows that the column density of methyl mercaptan in Ori A is less than 7×10^{13} cm^{-2}.

To summarize, the familiar sulfur molecule methyl mercaptan has been detected in Sgr B2 at roughly the level expected from the cosmic ratio of sulfur to oxygen. The rotational excitation of methyl mercaptan in this source appears to be approximately thermal at a rather low rotational temperature (about 9 K). Whether 9 K is also the kinetic temperature of the CH$_3$SH source, or the rotational excitation is instead subthermal, is unknown.

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